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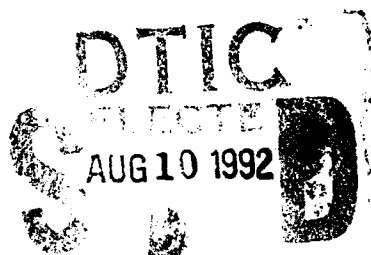
**SYNTHESIS OF BIS-(TRIFLUOROMETHYL) TRISULFIDE AND
BIS-(TRIFLUOROMETHYLTHIO) SELENIDE**

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RESEARCH DIRECTORATE



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13. ABSTRACT (Maximum 200 words) The reaction of trifluoromethylsulphenyl chloride with hydrogen sulfide at -78 °C and in the presence of a catalyst, namely 4-dimethylaminopyridine, furnished excellent yields of the desired bis-(trifluoromethyl) trisulfide in under 24 hrs. The previous preparation of this product required 30 days at room temperature. Bis-(trifluoromethyl) di- and pentasulfides were characterized as by-products by their gas chromatographic/mass spectrometric data. Replacement of the above catalyst with pyridine or N,N-dimethylaniline or triethylamine considerably reduced the yields of the expected product. Under similar experimental conditions, using hydrogen selenide bis-(trifluoromethylthio) selenide has been prepared for the first time. The structures assigned to these compounds have been confirmed by their mass spectral data.				
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Bis-(trifluoromethy) di- and pentasulfides

Dichlorofluoromethyl trifluoromethyl disulfide

PREFACE

The work described in this report was authorized under Project No. 1L162622A553, CB Defense/General Investigation. This work was started in March 1989 and completed in December 1990. The experimental data are recorded in laboratory notebook 88-0161.

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This report has been approved for release to the public.

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SYNTHESIS OF BIS-(TRIFLUOROMETHYL) TRISULFIDE AND BIS-(TRIFLUOROMETHYLTHIO) SELENIDE

1. INTRODUCTION:

In view of the wide occurrence of the di- and trisulfides in nature and the novel biological reactions associated with them, the chemistry of the polysulfides, in particular that of the S-S bond, has attracted considerable interest. These compounds have found application in energy transfer processes [1,2] and in the vulcanization of rubber [3]. Perfluoroalkyl groups, in particular, trifluoromethyl and trifluoromethylthio functionalities, exhibit unusual biological properties [4]. In fact, the incorporation of the latter group has been reported to considerably enhance the anti-psychotic properties of the parent compound [4b].

In connection with an on-going project [5a-b], bis-(trifluoromethyl) trisulfide (1) was required. An earlier preparation of 1 required thirty days at room temperature [6]. When a mixture of carbon disulfide and iodopentafluoride was heated at 200 °C, 1 was formed and characterized as one of the minor products of the reaction [6]. A 7 to 12% yield of 1 was obtained when a mixture of trifluoromethyl iodide and sulfur was heated at 310 °C for 36 hrs [6-8]. However, trifluoromethylsulfenyl chloride (2) reacted slowly with hydrogen sulfide (3) at room temperature to furnish acceptable yields of 1 [6]. The reaction of trifluoromethylchloro disulfide, obtained by the photolysis of a mixture of bis-(trifluoromethyl) disulfide (4) and sulfur dichloride (5), with trifluoromethylthiol (6) has been described to yield 1 [9]. Trifluoromethyl radicals, generated from a glow-discharge of hexafluoroethane, reacted with sulfur vapor exposed to radio frequency to give polysulfides containing 1 and carbon disulfide [8].

We now wish to report that the use of 4-dimethylaminopyridine (7) as a catalyst in the reaction of 2 with 3 at -78 °C furnishes 1 in satisfactory yields (75-80%), accompanied by trace amounts of the corresponding di-, tetra- and pentasulfides. Recently, we have developed and described an efficient method for the synthesis trifluoromethylthio-copper (8) in a crystalline form [10]. The reaction of 5 with 8 at room temperature for 45 minutes also gives 1 in a slightly reduced yield, accompanied by di- and polysulfides. Replacement of 7 with either pyridine, or N, N-dimethyl-aniline or triethylamine as a catalyst resulted in a considerably lower yield of 1. In fact, the reaction of 2 with 3 using triethylamine as a catalyst gave a complex mixture containing twelve

components. Substitution of 3 with hydrogen selenide (9) in the above preparation gave the selenium analog of 1, namely bis-(trifluoromethylthio) selenide (10). Dichloro-fluoromethyl trifluoromethyl disulfide (11) and 4 were identified as impurities accompanying 9. Table 1 describes the by-products of the reaction of 2 with 3 and 9 and of 5 with 8.

2. EXPERIMENTAL PART:

2.1 General Procedure: Warning!! Because of the high toxicity associated with 1 via inhalation, extreme care should be exercised in working with it and all reactions should be carried out in efficient hoods. NMR spectra (^{13}C and ^{19}F) were recorded in CDCl_3 on a Varian VXR-400S spectrometer at 100 MHz and 376 MHz respectively. The external reference for the ^{19}F data was CCl_3F . Mass spectra were obtained on a Finnigan Model 5100 GC/MS equipped with a silica 25 m x 0.31 mm. i.d. SE-54 capillary column (J and W Scientific, Rancho Cordova, CA). Routine GC analyses were accomplished with a Hewlett-Packard 5890A gas chromatograph equipped with a 30 m x 0.53 mm i.d. DB-5 column (J and W Scientific, Folsom, CA). The solvents were dried and freshly distilled before use. The reactions were carried out in a flame dried, argon purged 10 or 25 ml three-necked round bottom flask equipped with a magnetic stirrer, a gas inlet, a pressure equalizing dropping funnel and a reflux condenser carrying a dry ice-acetone trap. The temperature of the coolant passing through the reflux condenser was maintained at $-20\text{ }^\circ\text{C}$. After the reaction was over, the mixture was cooled to room temperature, flash distilled under reduced pressure, the distillate collected into a receiver cooled to $-78\text{ }^\circ\text{C}$, and finally fractionally distilled through a silvered, vacuum jacketed metal helix packed column.

2.2 Bis-(trifluoromethyl) trisulfide (1): Hydrogen sulfide (3) (0.68 gm., 0.02 mole) was sparged into a solution of 2 (5.4 gm., 0.027 mole) in freshly distilled, dry methylene chloride (5 mL) cooled to $-78\text{ }^\circ\text{C}$. A solution of 7 (1.2 gm., 0.01 mole) in dry methylene chloride was added dropwise. The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for two hrs and then at ambient temperature for one half hour. GC/MS analysis of the crude distillate obtained by flash distillation indicated the presence of bis-(trifluoro-methyl) di-, tetra- and pentasulfides in addition to the expected product. The crude distilled material was processed as described above to give a colorless liquid, b.p. $85\text{--}87\text{ }^\circ\text{C}$ (lit. [6] $86.2\text{ }^\circ\text{C}$) in 75% yield and a purity of 96% by glc (retention time=1.5 min). NMR: ^{13}C : $\delta = 128.7$

quartet); $J = 314 \pm 1$ Hz (Fig. 1). ^{19}F $\delta = 44.5$ (singlet) (Fig. 2). MS: $[\text{M}^+] = 234$; 215(M-F); 165(M-CF₃); 133(M-SCF₃); 96(SSS); 82(CSF₂); 69(CF₃); and 64(SS) (Fig. 3).

2.3 Bis-(trifluoromethyl) trisulfide Using Trifluoromethylthiocopper: A solution of sulfur dichloride (5) (3.1 gm., 80%, 0.024 mole) in 5 mL of dry xylene was added dropwise to a slurry of trifluoromethylthiocopper (8) (3.1 gm., 0.19 mole) in 5 mL of dry xylene at ambient temperature. The reaction was exothermic. After the addition was complete, the reaction was stirred for an additional thirty to fortyfive minutes and flashed distilled into a dry ice/acetone cooled receiver. GC/MS examination of the crude distillate indicated the presence of the di-, tetra- and pentasulfide as minor impurities. Further purification furnished the desired product (61%).

2.4 Bis-(trifluoromethylthio) selenide (10): To a solution containing 2 (5.4 gm., 0.27 mole) and hydrogen selenide (0.8 gm., 0.01 mole) in 5 mL of dry methylene chloride cooled to -78°C , was added with stirring, a solution of 7 (1.2 gm., 0.01 mole) in 5 mL of dry methylene chloride. After the addition was complete, the reaction mixture was allowed to warm to ambient temperature. The reaction mixture, after flash distillation under reduced pressure, was further fractionally distilled to yield the title compound in 86% yield, b.p. $100-102^\circ\text{C}$ with a purity of 94% by glc (retention time=8.4 min). NMR: ^{13}C : $\delta = 128.6$ (quartet); $J = 312.5 \pm 1$ Hz (Fig. 4). ^{19}F $\delta = 41.5$ (singlet) (Fig. 5). MS: $[\text{M}^+] = 282$; 263 (M-F); 213(M-CF₃); 101(SCF₃); 82(CSF₂); 69(CF₃); 63(CSF); 50(CF₂); and 32(S) (Fig. 6).

3. RESULTS AND DISCUSSION:

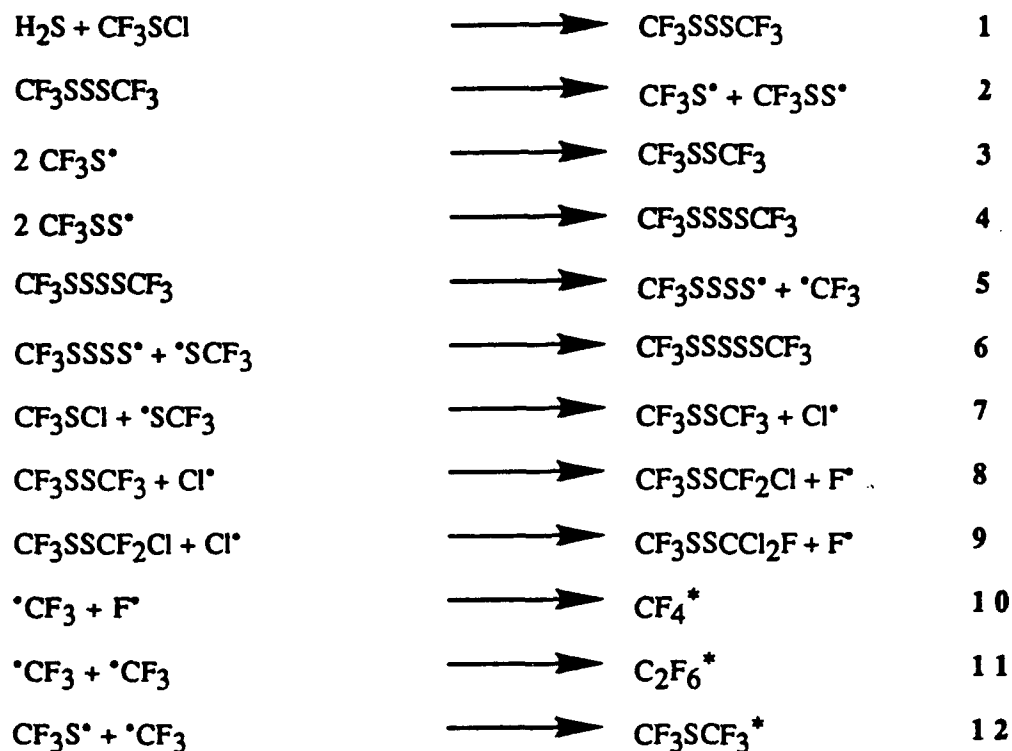
Table 1 lists, in addition to the expected products (1 and 10), the various by-products that have been identified from their mass spectral fragmentation patterns. The examination of the origin, formation and distribution of the by-products listed in Table 1 clearly suggests the involvement of free radicals in these reactions. It has been reported that the reaction between carbon disulfide and iodopentafluoride follows a free radical process [5]. A similar suggestion has been made about the reaction between trifluoromethyl iodide and sulfur [7]. Scheme 1 attempts to rationalize the origin and formation of the polysulfides and 11 identified by the GC/MS examination of the flash-distillate of the reaction mixture.

In a sense, Scheme 1 is an extension of an earlier suggestion [6] made to account for the formation of tri- and tetrasulfides. The disulfide, 4, is a ubiquitous product of the reaction of trifluoromethylthiocopper (8) with various substrates [11]. It is often accompanied by polysulfides. All of the compounds listed in Steps 1-6 have been characterized by their mass spectral fragmentation patterns. Steps 7-9 describe the formation of 11, initiated by the attack of the trifluoromethylthiyl radical on 2. The structure of 11 has been confirmed by its mass spectral fragmentation data. Tetrafluoromethane, hexafluoroethane and bis-(trifluoromethyl) sulfide (4) (Steps 10-12), though in principle should have been formed, were not detected. Even though they were formed, they could have been blown away by argon gas passing through the reaction mixture. C^o else, the origin of 11 may be 2 itself (Scheme 2), instead of Steps 8-9 of Scheme 1. The initially formed difluoromethylenesulfenyl chloride radical (Step 1 of Scheme 2) may undergo a rearrangement to give the thiyl radical. There are precedents for this type of rearrangement [12]. The rest of the free radical process (Steps 3-6) follows the accepted course.

The ¹³C and ¹⁹F chemical shifts of 1 and 10 are consistent with the structure assigned to these compounds. The introduction of Se in 10, shifted the ¹⁹F signal upfield by about 3 ppm, whereas the ¹³C chemical shift is unaffected. The ¹⁹F chemical shift of bis-(trifluoromethyl) disulfide itself appears as a singlet at 46.0 ppm [13]. Thus, the insertion of Se into the sulfur-sulfur bond of the disulfide to form 10, elicits a more pronounced effect on the ¹⁹F chemical shift than does the insertion of S to yield 1.

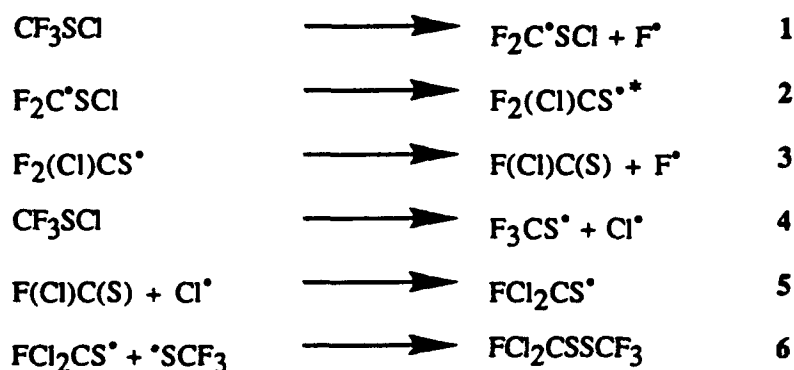
The polysulfides give the parent ion peak [M⁺] and the ion corresponding to m/e = 69 [CF₃]⁺. Other peaks which are conspicuously present are: [CF₃SSS]⁺ (m/e = 165); [CF₃SS]⁺ (m/e = 133); [CF₃S]⁺ (m/e = 101) and [CSF₂]⁺ (m/e = 82). Their mass spectra have already been reported by others [8, 14]. The prominent peaks in the mass spectrum of 11 are: [M⁺] = 234; 199 (M-Cl); 133 (M-SCF₃); 101 (SCF₃); 69 (CF₃); 63 (CSF); and 44 (CS).

Scheme 1: Genesis of Bis-(trifluoromethyl) di- and polysulfides.



* Were not detected.

Scheme 2: Postulated Route to Dichlorofluoromethyltrifluoromethyl disulfide.



*Undergoes a rearrangement.

4. CONCLUSIONS:

In the presence of the catalyst, 4-dimethylaminopyridine, the reaction of trifluoromethylsulfenyl chloride with hydrogen sulfide at -78°C gives excellent yields of bis-(trifluoromethyl) trisulfide in 24 hrs. Bis-(trifluoromethyl) di-, tetra- and pentasulfides accompany the trisulfide as minor products. An earlier preparation of the trisulfide required 30 days. Using this procedure, bis-(trifluoromethylthio) selenide has been prepared for the first time. The influence of other catalysts on the course of the reaction, the formation of unusual by-products, and the mass spectral fragmentation data are presented in this communication. A new procedure has been developed for the synthesis of the title compounds and the participation of free radicals has been invoked to rationalize the formation of the by-products of the reaction.

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  at   1.000      PROCESSING
  ap   20000 lb      1.00
  av   25000.0 f4    65536
  rb   13800 math    r
  ba   16
  pu   10.3 verr
  lpar not used wosp
  d1    2.000 ubo      wft
  tot   1000.0 unl
  nt    10.06
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  l2     a hzam    80.46
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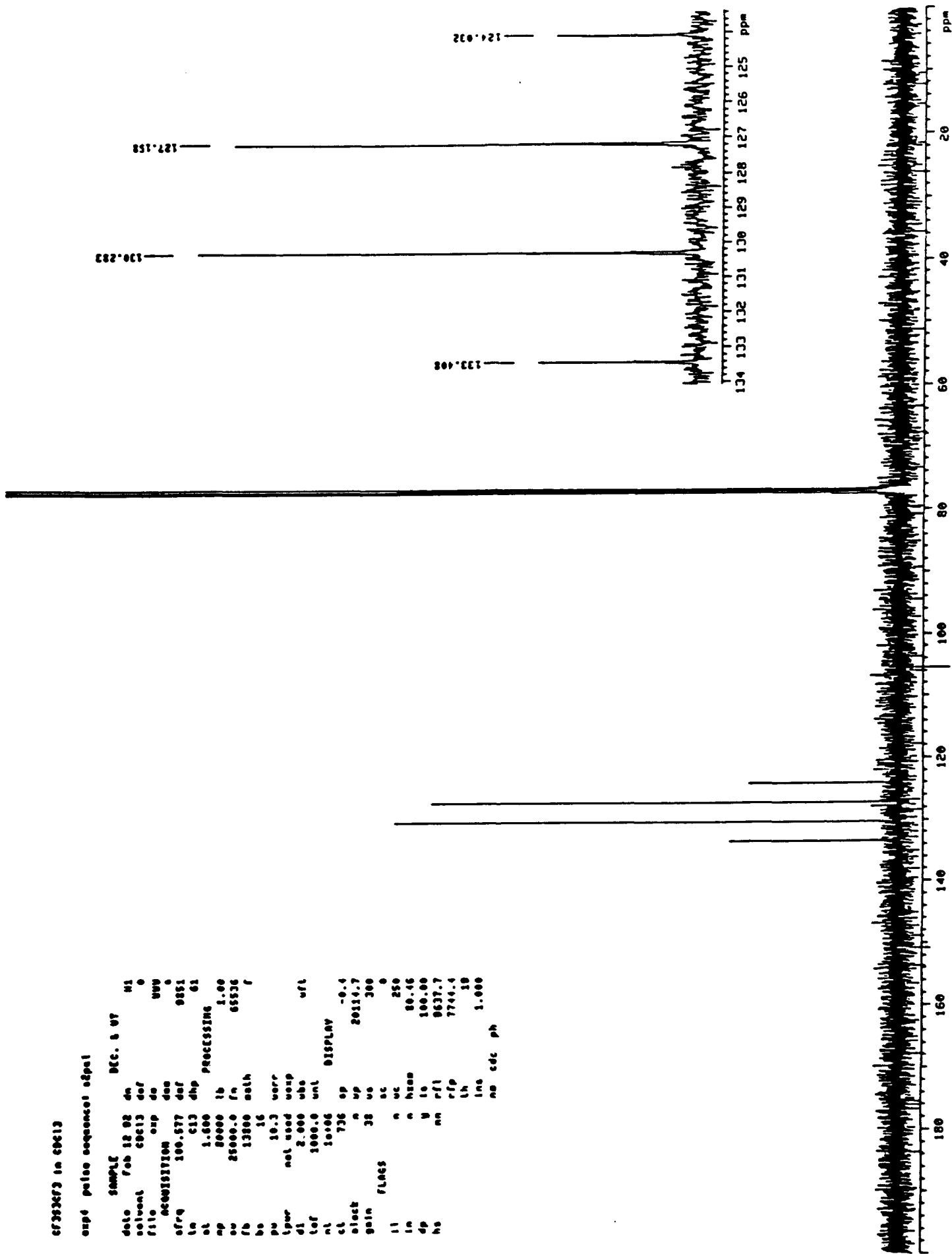


Figure 1: ¹³C-NMR of Bis-(trifluoromethyl) trisulfide

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pu	15.0	corr		
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ct	20	unt		
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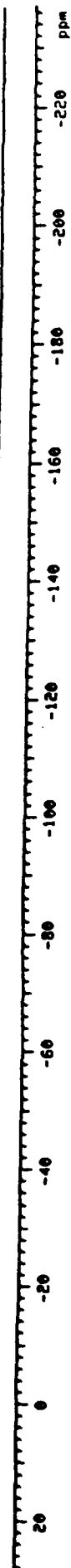


Figure 2: ^{19}F -NMR of Bis-(trifluoromethyl) trisulfide

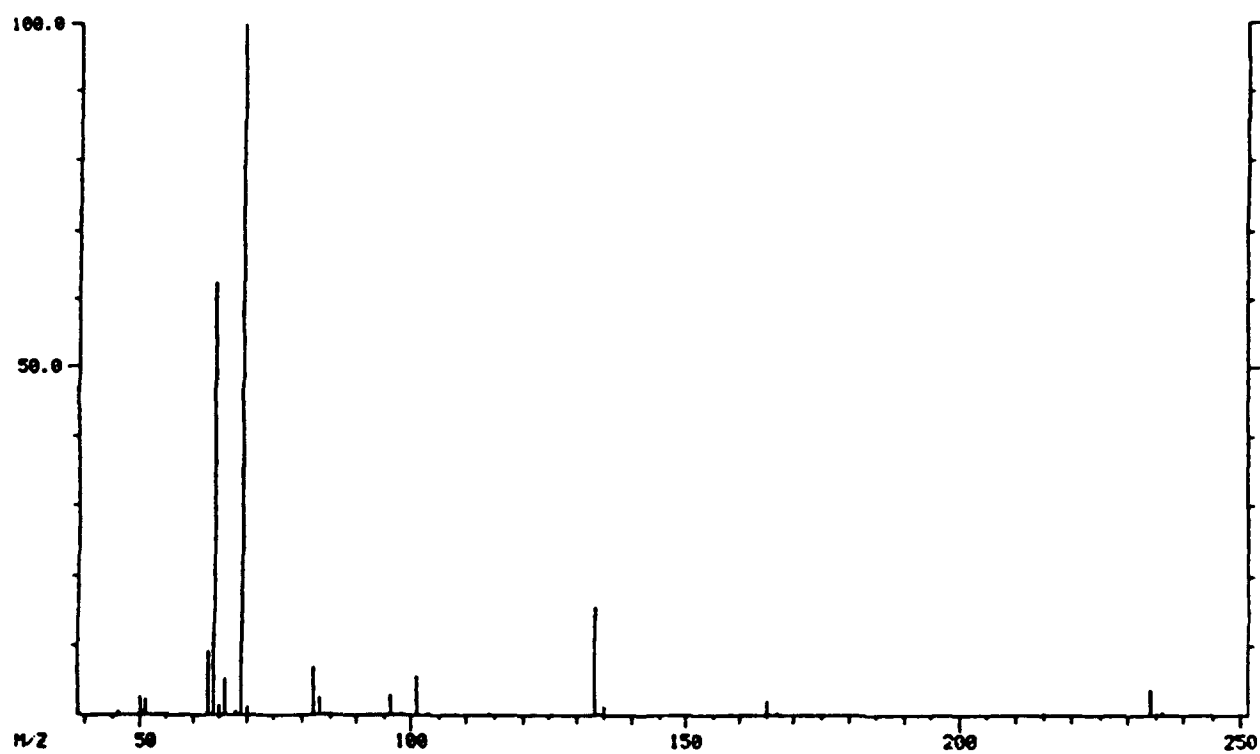


Figure 3: Mass Spectrum of Bis-(trifluoromethyl) trisulfide

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 as 25000.0 fa 65536
 ab 13800 nalk
 ba 16
 pa 10.3 verr
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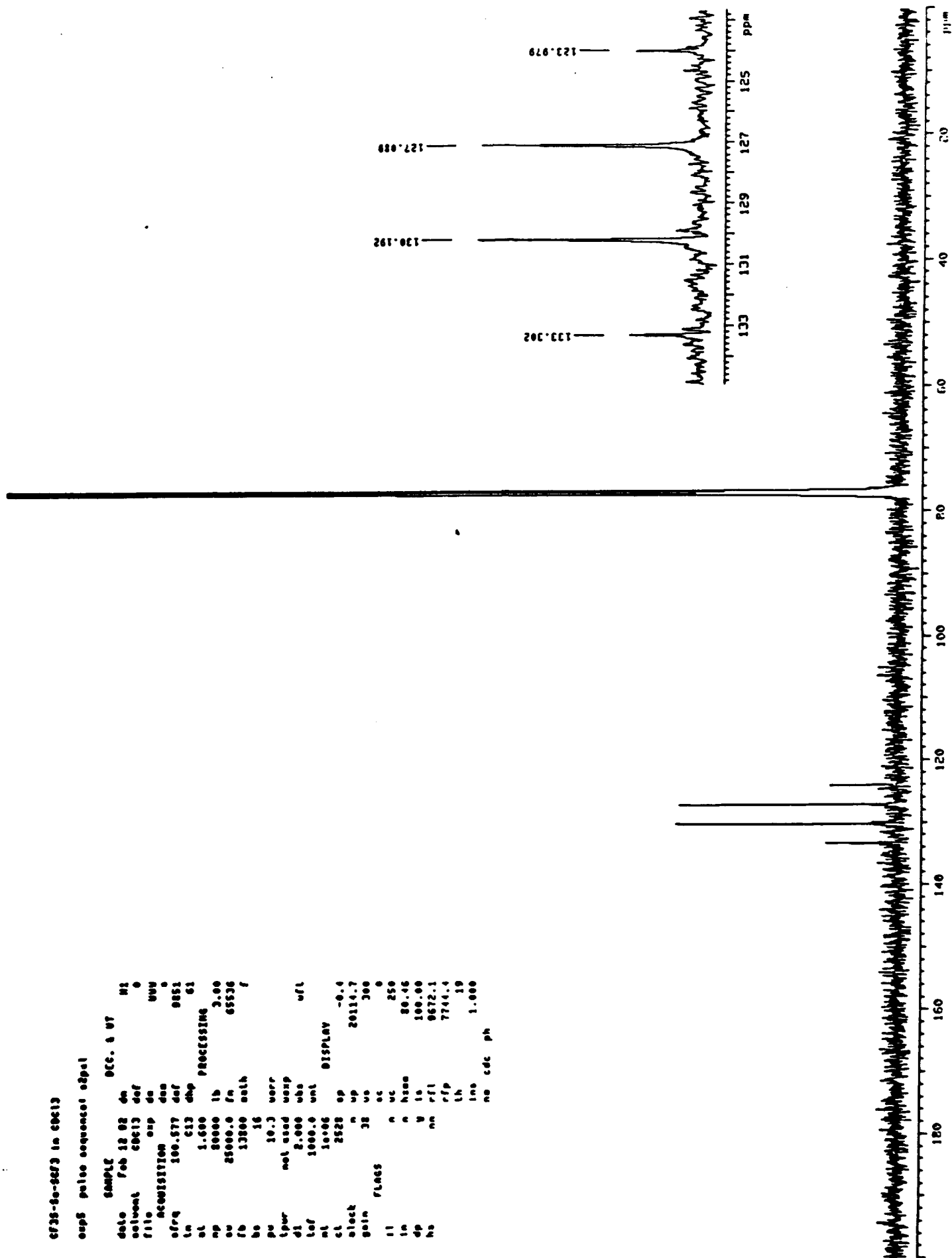


Figure 4: ^{13}C -NMR of Bis-(trifluoromethyl) trisulfide

0930-60-0073 in c0013

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pw       15.0
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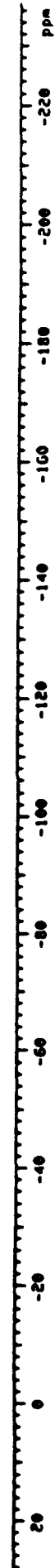


Figure 5: ^{19}F -NMR of Bis-(trifluoromethylthio) selenide

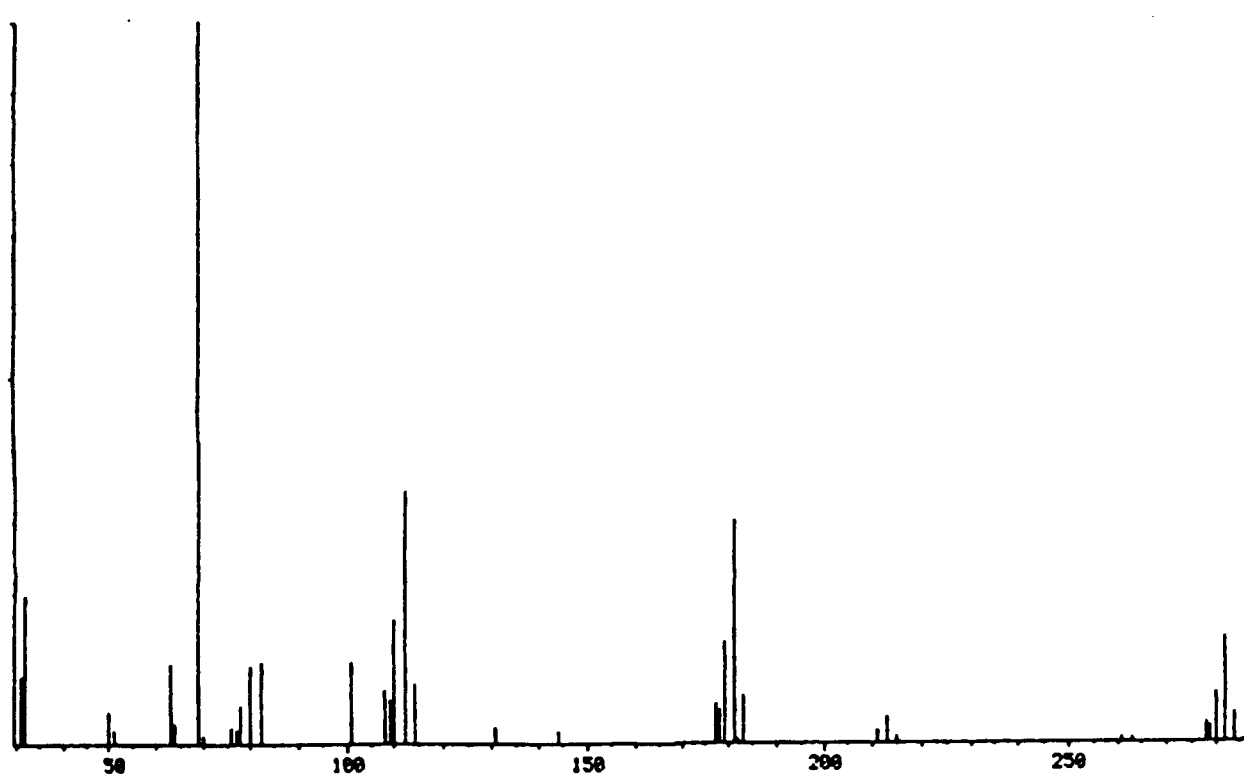


Figure 6: Mass Spectrum of Bis-(trifluoromethylthio) selenide

Table 1: By-products of the Reaction of Trifluoromethanesulfonyl chloride.

<u>Substrates</u>	<u>By-products</u>
H ₂ S	CF ₃ SSCFCl ₂ * + (CF ₃ S) ₂ * + (CF ₃ SS) ₂ S*
H ₂ Se	CF ₃ SSCFCl ₂ + (CF ₃ S) ₂
CF ₃ SCu	(CF ₃ S) ₂ + (CF ₃ SS) ₂ + (CF ₃ SS) ₂ S

* Were not detected in an earlier report [6].

Table 2: Mass Spectral Fragmentation of the Products Listed in Table 1.

(CF ₃ S) ₂ [R. T.*=1.18 min]	M ⁺ =202; 183(M-F); 133(CF ₃ SS); 114(CF ₃ SS); 101(CF ₃ S); 95(CFSS); 69(CF ₃ , 100 %); 64(SS); and 50(CF ₂).
(CF ₃ SS) ₂ [R. T.=3.1 min]	M ⁺ =266; 197(M-F); 165(CF ₃ SSS); 133(CF ₃ SS); 96(SSS); 82(CSF ₂); 69(CF ₃ , 100 %); 64(SS) and 50(CF ₂).
(CF ₃ SS) ₂ S [R. T =5.29 min.]	M ⁺ =298; 234(M-SS); 165(CF ₃ SSS); 133(CF ₃ SS); 69(CF ₃ , 100 %) and 64(SS, 100 %).
(CF ₃ SSCFCl ₂) [R. T.=8.9 min]	M ⁺ =234; 199(M-Cl); 133(M-SCF ₃); 101(SCF ₃); 69(CF ₃ , 100 %); 63(CSF) and 44(CS).

*=Retention Time.